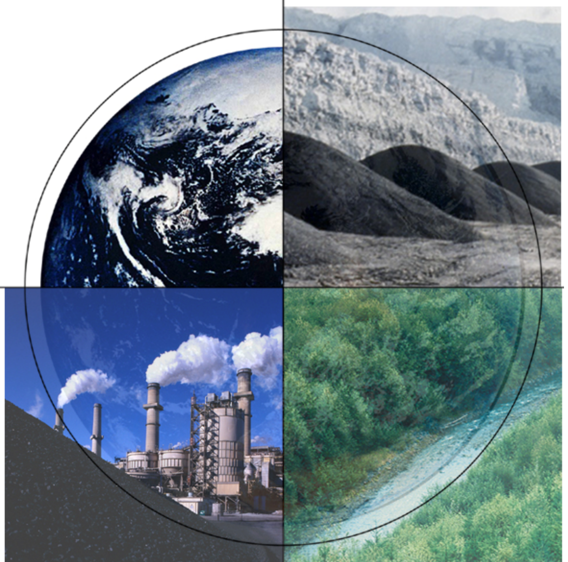
Mercury Control Program Review



The PCO Process for Removal of Mercury from Flue Gas

Christopher R. McLarnon, Evan J. Granite, and Henry W. Pennline

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National Energy Technology Laboratory

Office of Fossil Energy

GP-254 / PCO Process

- Alternative to ACI Developed
- Oxidation of Mercury
- Irradiation of Flue Gas with 254-nm Light
- 90% Oxidation Attained at Bench-Scale
- Low Parasitic Power (less than 0.5%)
- Patent Issued June 2003
- Licensed for Application to Coal-Burning Power Plants (Powerspan Corporation)
- Potential Application for Incinerators

Regulatory Drivers

- EPA Announcement March 15, 2005
- Clean Air Mercury Rule
- Several States Requiring Stricter Reductions
- 70-90% Removal Requirement
- Phased in Over Several Years

Fossil Energy Program Goals

Develop more effective mercury control options

- Cost-effective and high level of mercury removal
- Meet long-term IEP program goal of 90% mercury reduction at cost reduction of 25-50%
- Must be better than ACI

Technical Challenges

Mercury is Difficult to Capture

- Low concentration
- Exists as Hg^0
- Harsh conditions of coal-derived flue gas
- Competitive adsorption / poisoning
- Low sorbent reactivity
- Hg is semi-noble metal

ACI for Mercury Removal

- **Benchmark technology**
  - Deficiencies for flue gas applications
- **General adsorbent**
- **Limited temperature range**
- **Sequestration**
- **High sorbent / Hg ratio (3,000:1 to 100,000:1)**
- **Contacting methods**
- **Expensive: $1,000 - 3,000/ton**
- **500 MW_e power plant: $0.5 - 10 MM/yr**

Technical Challenges
Mercury is Difficult to Measure

- Low concentration & harsh conditions
- Exists as Hg, $HgCl_2$, and $Hg_{(particulate)}$
- Continuous conversion among three
- Broad-band absorbers
- Quenching
- Photosensitized oxidation
- Competitive adsorption/ poisoning

NETL

Background: GP-254 Process

Discovery

- Sorbent development
- UV measurement of mercury
- AFS
- Unwanted red-brown stains
- Mercuric oxide
- Serendipity

Photochemical Oxidation of Mercury

- Mercury can absorb and emit 253.7 nm light
- Atomic Absorption (AAS)

  $Hg + 253.7\ nm\ radiation \rightarrow Hg^{*} \quad Hg\ 6\ (^{3}P_{1}) \qquad (I)$

- Atomic Emission (AES)

  $Hg^{*} \rightarrow Hg + 253.7\ nm\ radiation \qquad (II)$

- Atomic Fluorescence (AFS): steps (I) and (II)
- Basis for CEMs

What Is Quenching?

- Intensity of fluorescent emission diminished
- Energy transfer due to collisions
- Function of size, shape, and reactivity
- Primed for chemical reaction (activation)
- Interferes with ultraviolet spectroscopy

$Hg + 253.7\ nm\ light \rightarrow Hg^*$	Hg 6 ($^3P_1$)
$Hg^* \rightarrow Hg + 253.7\ nm\ light$	Fluorescence
$Hg^* + M \rightarrow Hg + M^*$	Quenching

Quenching Cross Sections

$$Hg\ 6(^3P_1) + M \rightarrow Hg\ 6(^1S_0) + M^*$$

Function Of Size, Shape And Reactivity

Species	Cross Section (cm^2)
HCl	37.0×10^{-16}
NO	24.7×10^{-16}
O_2	13.9×10^{-16}
CO	4.1×10^{-16}
CO_2	2.5×10^{-16}
H_2O	1.0×10^{-16}
N_2	0.4×10^{-16}

Photochemical Oxidations

- First described in 1926 by Dickinson & Sherrill (O_2)
- Gunning discovered others in 1950s (HCl, H_2O, CO_2)

Relevant Overall Reactions

$Hg + 2\ O_2$ + 253.7 nm light $\rightarrow$ $HgO + O_3$

$Hg + HCl$ + 253.7 nm light $\rightarrow$ $HgCl + 1/2\ H_2$

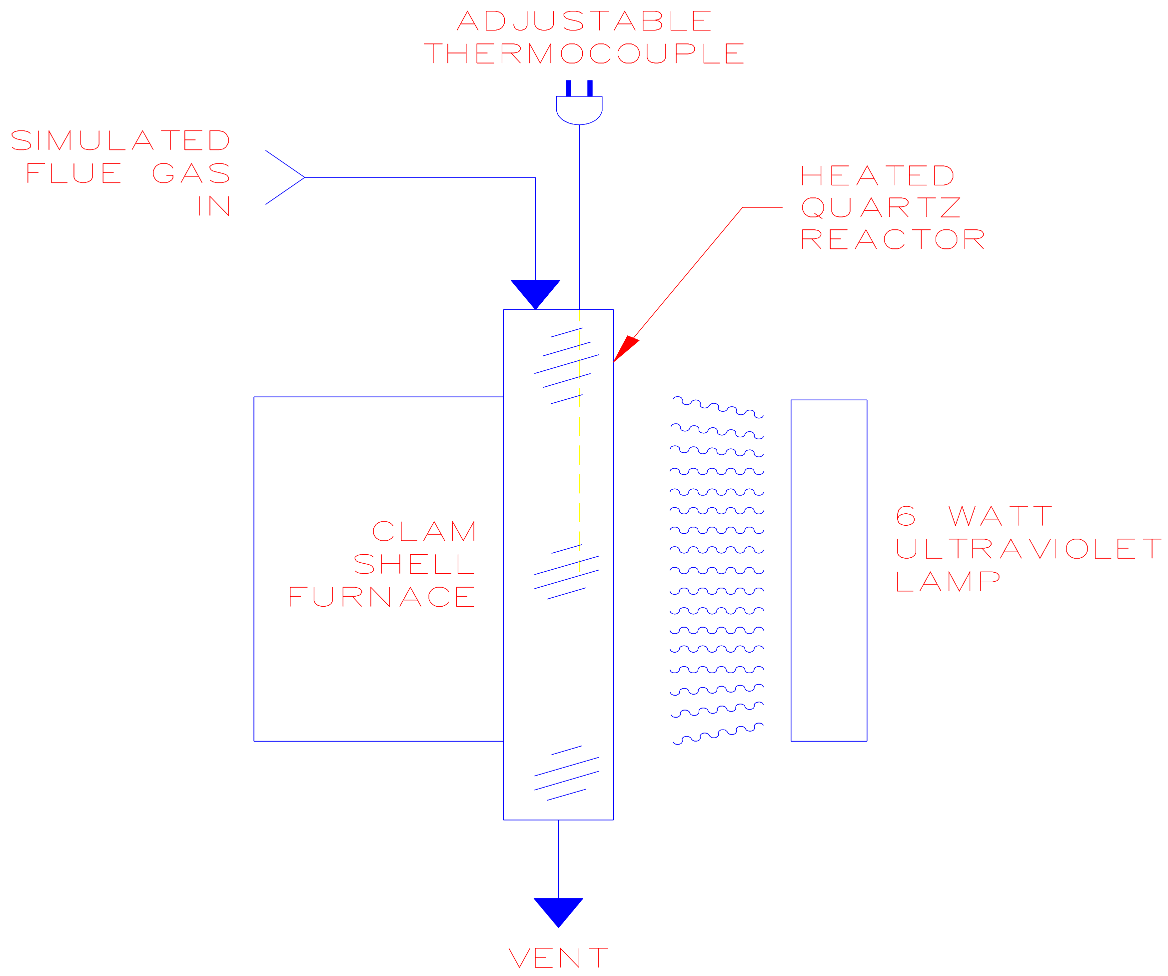
$Hg + H_2O$ + 253.7 nm light $\rightarrow$ $HgO + H_2$

$Hg + NO_2$ + 253.7 nm light $\rightarrow$ $HgO + NO$

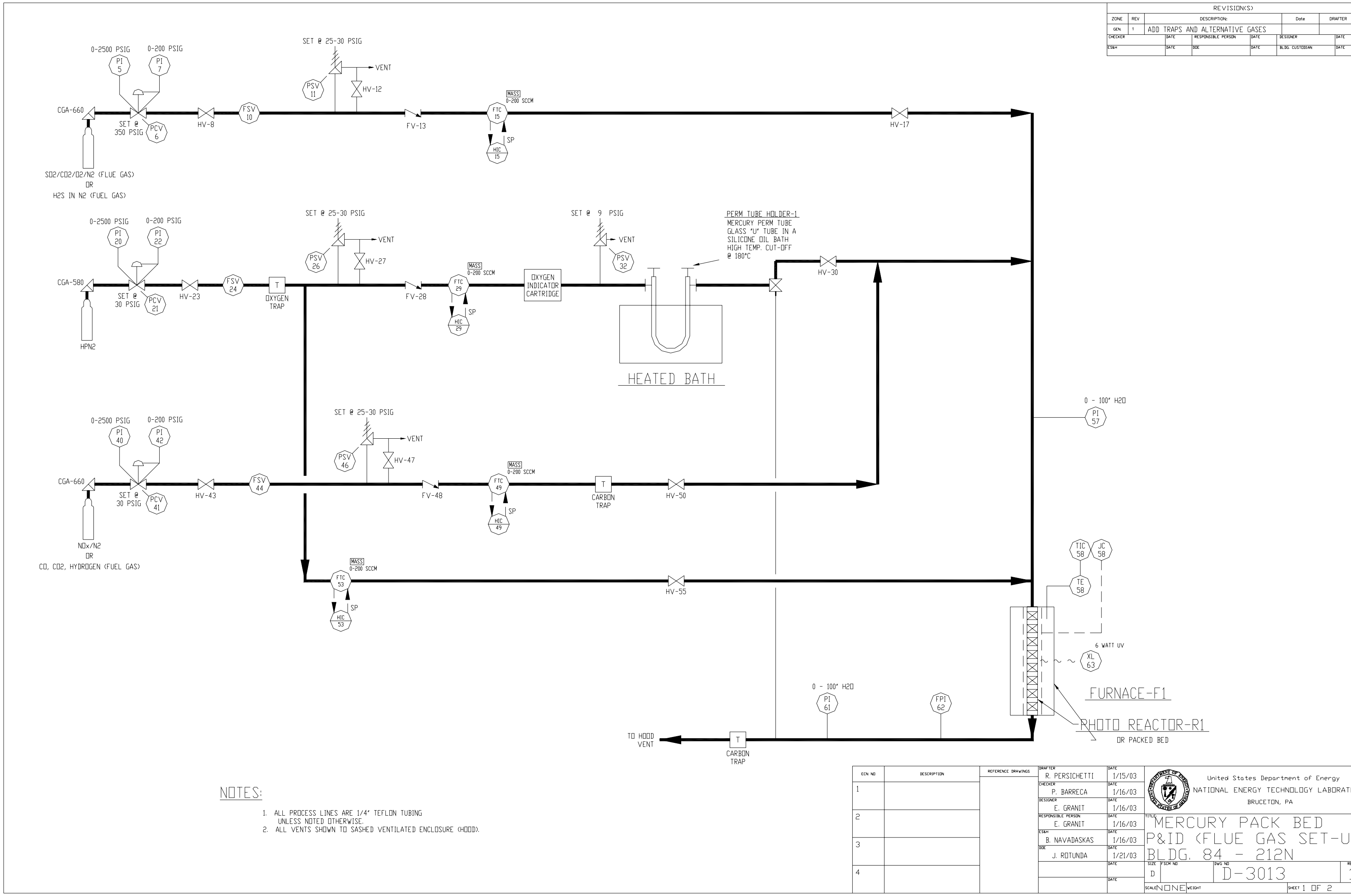
$Hg + CO_2$ + 253.7 nm light $\rightarrow$ $HgO + CO$

- Interferes with UV-based CEMs
- Potential removal method

Lab-Scale Photoreactor



Photoreactor for Removal of Mercury


REVISION(S)
ZONE REV DESCRIPTION: Date DRAFTER
GEN. 1 ADD TRAPS AND ALTERNATIVE GASES
0-2500 PSIG
0-200 PSIG
PI 5
PI 7
SET @ 25-30 PSIG
VENT
PSV 11
HV-12
CGA-660
SET @ 350 PSIG
PCV 6
HV-8
FSV 10
FV-13
MASS 0-200 SCCM
FTC 15
SP
HIC 15
HV-17
SO2/CO2/O2/N2 (FLUE GAS) OR H2S IN N2 (FUEL GAS)
PI 20
PI 22
SET @ 25-30 PSIG
PSV 26
HV-27
SET @ 9 PSIG
PSV 32
PERM TUBE HOLDER-1
MERCURY PERM TUBE GLASS "U" TUBE IN A SILICONE OIL BATH HIGH TEMP. CUT-OFF @ 180°C
CGA-580
SET @ 30 PSIG
PCV 21
HV-23
FSV 24
OXYGEN TRAP
FV-28
FTC 29
HIC 29
OXYGEN INDICATOR CARTRIDGE
HV-30
HPN2
HEATED BATH
0 - 100" H2O
PI 57
PI 40
PI 42
SET @ 25-30 PSIG
PSV 46
HV-47
CGA-660
SET @ 30 PSIG
PCV 41
HV-43
FSV 44
FV-48
FTC 49
HIC 49
CARBON TRAP
HV-50
NOx/N2 OR CO, CO2, HYDROGEN (FUEL GAS)
FTC 53
HIC 53
HV-55
TIC 58
JC 58
TE 58
6 WATT UV
XL 63
FURNACE-F1
PHOTO REACTOR-R1
OR PACKED BED
0 - 100" H2O
PI 61
FPI 62
TO HOOD VENT
CARBON TRAP
NOTES:
1. ALL PROCESS LINES ARE 1/4" TEFLON TUBING UNLESS NOTED OTHERWISE.
2. ALL VENTS SHOWN TO SASHED VENTILATED ENCLOSURE (HOOD).
ECN NO DESCRIPTION REFERENCE DRAWINGS
DRAFTER R. PERSICHETTI 1/15/03
CHECKER P. BARRECA 1/16/03
DESIGNER E. GRANIT 1/16/03
RESPONSIBLE PERSON E. GRANIT 1/16/03
ES&H B. NAVADASKAS 1/16/03
DOE J. ROTUNDA 1/21/03
United States Department of Energy
NATIONAL ENERGY TECHNOLOGY LABORATORY
BRUCETON, PA
MERCURY PACK BED P&ID (FLUE GAS SET-UP BLDG. 84 - 212N
SIZE D
DWG NO D-3013
REV 1
SCALE NONE
SHEET 1 OF 2

Experimental Parameters

- Quartz Photoreactor, 6-watt UV lamp
- Temperatures: 80^{o}F, 280^{o}F, 350^{o}F
- Flow-rate: 60 ml/min Reaction time: 350 min
- Intensity: 1.4 mW/cm^2

Gas Compositions

A: 16% CO_2, 5% O_2, 2000 ppm SO_2,
300 ppb Hg, balance N_2

B: 16% CO_2, 5% O_2, 2000 ppm SO_2,
500 ppm NO, 300 ppb Hg, balance N_2

Results: Photochemical Removal

Gas	Temp (°F)	Mean Hg Capture (%)
A	350	2.3 ± 2.0
A	280	71.6 ± 30.1
A	80	67.8 ± 28.8
B	280	26.8 ± 11.7

- Removal as mercuric oxide/mercurous sulfate stain
- Higher removals below 300°F
- Limited by thermal decomposition of O_3 (300-350°F)
- NO reduces removal, possibly by consuming ozone
- Low energy consumption
- Potentially low operating costs

Conclusions: Photochemical Oxidation

Method For Mercury Removal

- Obvious interference For CEMs
- High levels of mercury removal from SFG
- Capture as HgO and Hg_2SO_4
- Enhanced removal below 300ºF

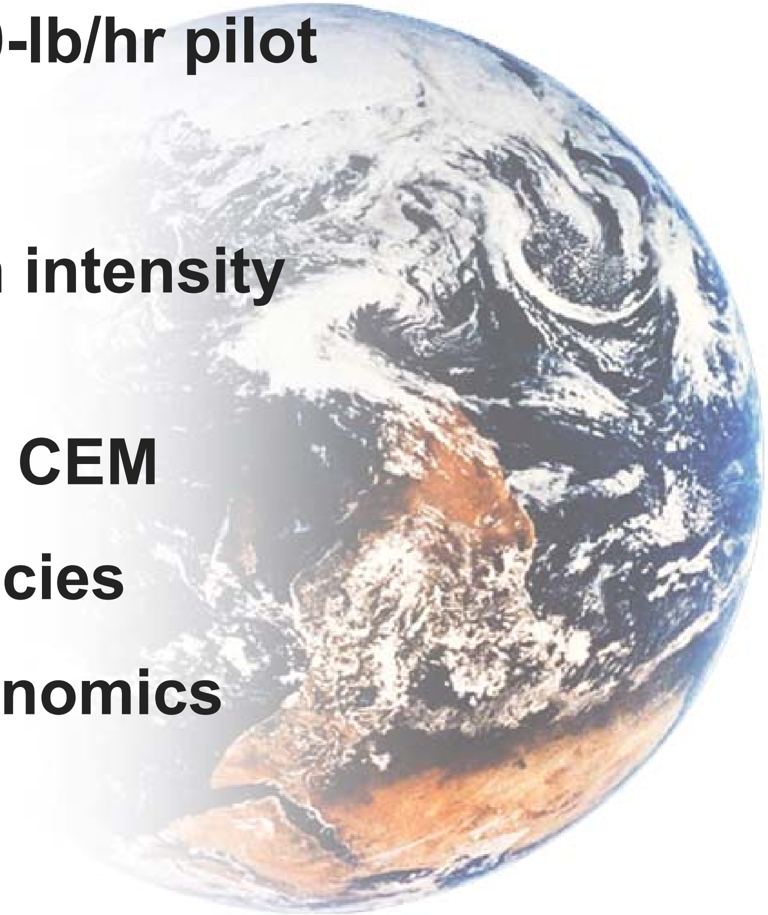
Conclusions: Photochemical Oxidation

Potential For Better Performance

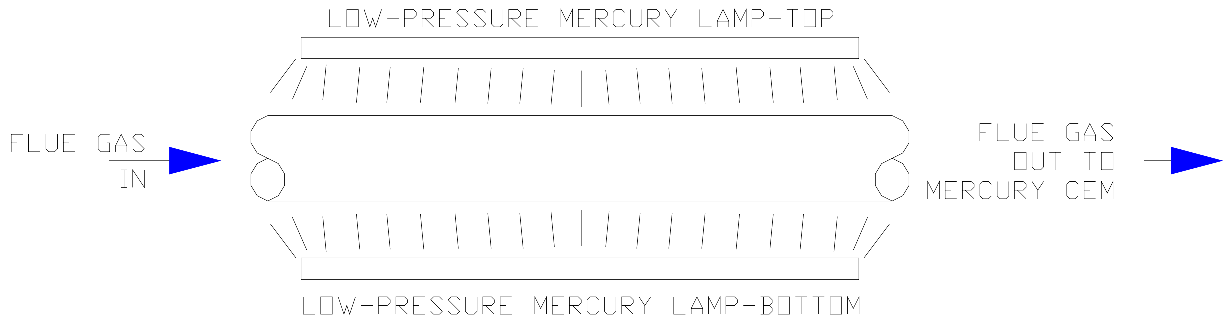
- Other oxidants (HCl, H_2O, NO_2) in flue gas
- Promising process economics
- Potential for multi-pollutant control
- Pilot-scale data needed
- Low rank coals are of particular interest

Larger Scale Testing
Bench-Scale Photoreactor

- Slipstream of flue gas from 500-lb/hr pilot
- Temperature: 280ºF - 350ºF
- Effect of temperature, radiation intensity residence time & composition
- Removals measured on-line by CEM
- Impact upon other flue gas species
- Determine GP-254 process economics



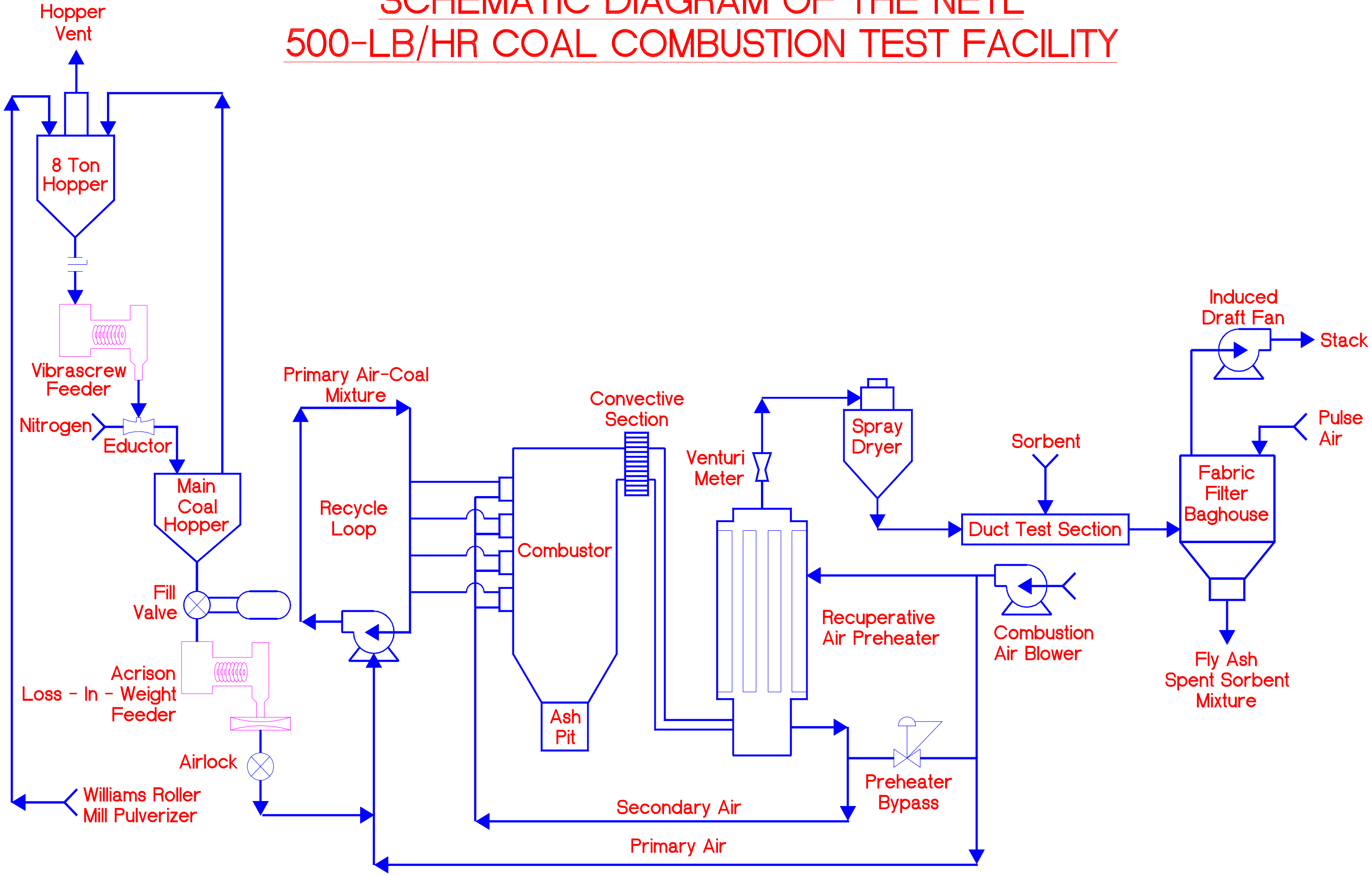
NETL BENCH-SCALE PHOTOREACTOR



NETL Bench-Scale Photoreactor

- ½-inch by 33-inch Quartz Tube
- Two 30-W Low Pressure Mercury Lamps
- 254-nm Intensity: 20 mw/cm^2
- Gas Composition: PRB Flue Gas
- Temperature: 120°F - 280°F
- Flow-Rate: 8 liters/min
- Sir Galahad CEM Monitor Inlet/Outlet Mercury

SCHEMATIC DIAGRAM OF THE NETL 500-LB/HR COAL COMBUSTION TEST FACILITY



NETL Bench-Scale Results

Significant Level of Mercury Oxidation

- **Slipstream of Particulate-Free PRB Flue Gas**
- **6 – 50 µg/Nm^3 Elemental Mercury (Spiking)**
- **Low Power Consumption**
- **Typically 30-70% Removal of Mercury**
- **Extremely Low UV Intensity Applied**
- **Non-Optimized Bench-Scale Apparatus**

Powerspan Bench-Scale Results

Commercial Lamp System

- Flow-rate: 24 scfm
- Temperature: 120 - 140°F
- Intensity: 13.8 W/cm^2 -- Low Parasitic Power
- Mercury Concentration: 13.0 µg/Nm^3
- 5.6% O_2, 13% CO_2, 8% H_2O, 1300 ppm SO_2, 220 ppm NO, 20 ppm CO, and balance N_2
- 91% Removal
- Pilot-Scale Tests in 2005